

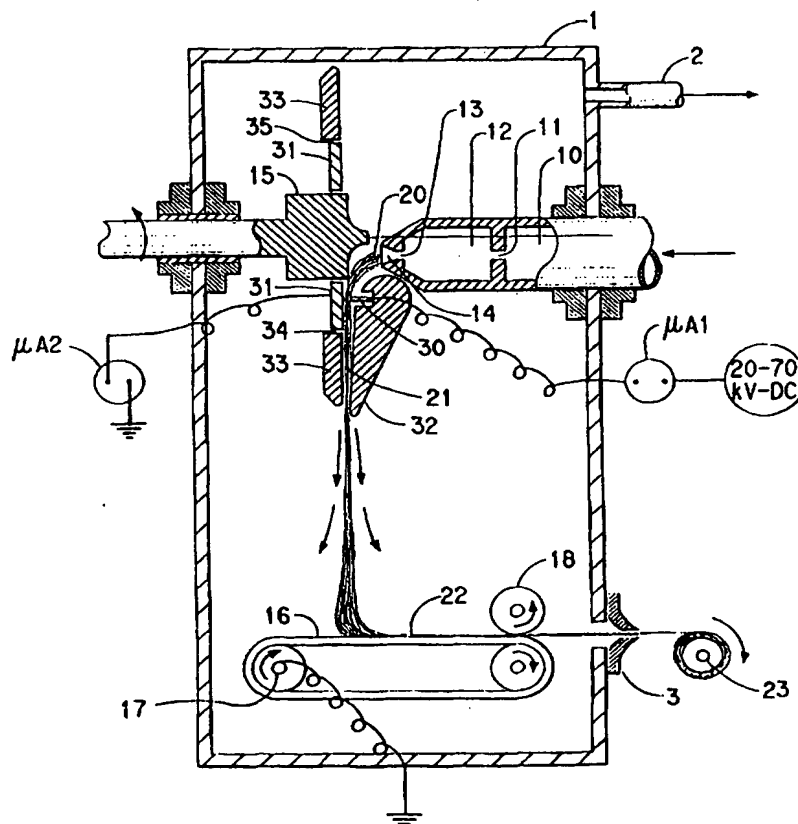
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(54) Title: FLASH-SPUN POLYMER

## (57) Abstract

This invention relates to significant improvements in tensile, elongation and toughness properties of flash-spun fibers and nonwoven sheets made from flash-spun fibers. The invention is directed to improved fiber and sheet properties with narrow molecular weight distribution polyethylene and further improvements when combined with process aspects.



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## FLASH-SPUN POLYMER

## Field of the Invention

This invention relates to flash spinning polymer and particularly  
5 to the products made from flash spinning polymer such as fibrous webs and  
consolidated sheets and fabrics.

## Background of the Invention

Flash-spun fibers were originally created by Herbert Blades and James White, employees of E. I. du Pont de Nemours and Company (DuPont), and disclosed in US Patent 3,081,510 on 19 March 1962. A variety of polymeric materials were disclosed in the patent primarily including linear polyethylene with some examples of polypropylene. Further examples of polymeric materials which may be spun into plexifilaments were described in a subsequent patent, US Patent 3,227,784 on 4 January 1966, also to Blades et al. These included polyethylene terephthalate, polytetramethylbutadiene, polyhexamethylene adipamide, polyformaldehyde resin, and perfluoroethylene/perfluoropropylene copolymer in addition to further examples of linear polyethylene and polypropylene.

Based upon the developments of Blades and White, and subsequent work of others, DuPont has scaled up to commercial production of flash-spun products under the trademark Tyvek® spunbonded olefin. Tyvek® spunbonded olefin has many uses for which its properties have been adapted and engineered such as air infiltration barriers, banners, envelopes, medical packaging, and protective apparel. DuPont has developed two basic styles of flash-spun nonwoven sheet products: area bonded material and point bonded material. Area bonded material is thermally bonded generally uniformly across the area of the sheet. Point or pattern bonded material is thermally bonded at points or in a pattern where the pattern creates portions which are more strongly bonded and not as strongly bonded. As such, area bonded products are typically stiffer than point bonded and have a paper-like feel. Point bonded flash-spun nonwoven

products tend to have softer fabric-like feel. Point bonded flash-spun material is most commonly used in protective apparel. Area bonded products are used in envelopes, medical packaging and air infiltration barriers in construction applications.

5           In several end uses, the tensile and elongation properties of the flash-spun nonwoven fabrics are of considerable importance such as in packaging and protective apparel. For example, the material for protective apparel is preferably quite strong; however, if it were to fail, then it is  
10       desired that it fail by stretching and deforming rather than ripping or breaking. It is particularly desirable that both tensile strength and elongation are high at the same time.

Thus, it is an object of the present invention to improve the tensile and elongation properties of flash-spun products.

15       It is a further object to provide better quality flash-spun fibers and sheet products made from flash-spun fibers.

#### Summary of the Invention

In the present invention, the foregoing objects are achieved by a polyethylene flash-spun plexifilamentary film-fibril material having a BET surface area of at least about two m<sup>2</sup>/gm and wherein the polymer has a  
20       number average molecular weight of at least about 20,000 and a molecular weight distribution of less than 4.0.

#### Brief Description of the Drawings

The invention will be more easily understood by a detailed explanation of the invention including drawings. Accordingly, drawings  
25       which are particularly suited for explaining the invention are attached herewith; however, it should be understood that such drawings are for explanation only and are not necessarily to scale. The drawings are briefly described as follows:

30       Figure 1 is a schematic view of an apparatus suitable in the process of flash spinning polymer into a plexifilamentary web and laying down the plexifilamentary web to form a nonwoven sheet:

Figure 2 is a fragmentary perspective view of the laydown of the plexifilamentary web in Figure 1;

Figure 3 is an enlarged cross sectional view of the letdown chamber and spin orifice in the apparatus in Figure 1; and

5 Figure 4 is a schematic view of a small scale test system for making plexifilamentary yarn from polymer.

#### Detailed Description of the Preferred Embodiment

Referring now to the drawings, a preferred system and process for flash spinning fibers and forming sheets is illustrated in Figures 1 and 2.

10 The basic system has been previously disclosed in U.S. Patent 3,860,369 to Brethauer et al., which is hereby incorporated by reference. The process is conducted in a chamber 1, sometimes referred to as a spin cell by those in the industry, which has a vapor-removal port 2 and an opening 3 through which non-woven sheet material produced in the process is removed.

15 Polymer solution (or spin liquid) is continuously or batch-wise prepared at an elevated temperature and pressure and provided to the spin cell 1 via a conduit 10. The pressure of the solution is greater than cloud-point pressure which is the lowest pressure at which the polymer is fully dissolved in the spin agent forming a homogeneous single phase mixture.

20 The single phase polymer solution passes through a letdown orifice 11 into a lower pressure (or letdown) chamber 12. In the lower pressure chamber 12, the solution separates into a two-phase liquid-liquid dispersion. One phase of the dispersion is a spin agent-rich phase which comprises primarily spin agent and the other phase of the dispersion is a polymer-rich phase which contains most of the polymer. This two phase  
25 liquid-liquid dispersion is forced through a spinneret 13 into an area of much lower pressure (preferably atmospheric pressure) where the spin agent evaporates very rapidly (flashes), and the polyolefin emerges from the spinneret as a yarn (or plexifilament) 20. The yarn 20 is stretched in a tunnel  
30 14 and is directed to impact a rotating baffle 15. The rotating baffle 15 has a shape that transforms the yarn 20 into a flat web 21, which is about 5-15 cm wide, and separating the fibrils to open up the web 21. The rotating baffle 15 further imparts a back and forth oscillating motion having sufficient

amplitude to generate a wide back and forth swath. The web 21 is laid down on a moving wire laydown belt 16 located about 50 cm below the spinneret 13, and as best seen in Figure 2, the back and forth oscillating motion is arranged to be generally across the belt 16 to form a sheet 22.

5           As the web 21 is deflected by the baffle 15 on its way to the moving belt 16, it enters a corona charging zone between a stationary multi-needle ion gun 30 and a grounded rotating target plate 31. The multi-needle ion gun 30 is charged to a DC potential by a suitable voltage source 36. The charged web 21 is carried by a high velocity spin agent vapor stream  
10 through a diffuser consisting of two parts: a front section 32 and a back section 33. The diffuser controls the expansion of the web 21 and slows it down. The back section 33 of the diffuser may be stationary and separate from target plate 31, or it may be integral with it. In the case where the back section 33 and the target plate 31 are integral, they rotate together. Figure 1  
15 shows the target plate 31 and the back section 33 of the diffuser as a single unit. Aspiration holes 34 and 35 are drilled in the back section 33 of the diffuser to assure adequate flow of gas between the moving web 21 and the diffuser back section 33 to prevent sticking of the moving web 21 to the diffuser back section 33. The moving belt 16 is grounded through roll 17 so  
20 that the charged web 21 is electrostatically attracted to the belt 16 and held in place thereon. Overlapping web swaths collected on the moving belt 16 and held there by electrostatic forces are formed into a sheet 22 with a thickness controlled by the belt speed. The sheet 22 is compressed between belt 16 and consolidation roll 18 into a structure having sufficient strength to  
25 be handled outside the chamber 1 and then collected outside the chamber 1 on a windup roll 23.

Flash-spun nonwoven sheets made by a process similar to the foregoing process are sold as Tyvek® spunbonded olefin sheets for air infiltration barriers in construction applications, as packaging such as air  
30 express envelopes, as medical packaging, as banners, and for protective apparel and other uses. Tyvek® spunbonded olefin is quite strong and lightweight with small interstices between the fibers to allow moisture vapor and air to permeate the sheet but limit passage of liquid water.

Thus, the properties of Tyvek® spunbonded olefin is of considerable interest and importance for its various end uses. It should go without saying that it is always desirable to improve the properties of flash-spun products as long as there is not a sacrifice of other important properties. As described in many prior patent applications on flash spinning, a myriad of variations have been disclosed that lead to variations in properties of flash-spun fabrics.

One particular important set of properties of Tyvek® spunbonded olefin sheet are tensile strength, elongation and toughness. Tyvek® spunbonded olefin has considerable tensile strength especially considering that it is made of high density polyethylene. Flash spinning tends to provide highly oriented polymer in the plexifilaments. While flash spinning provides good tensile properties, improved tensile properties as well as considerable elongation and toughness would be appreciated in the market place. Elongation is a measure of the amount the product stretches before it breaks. Work to Break (WTB) relates to both the elongation and tensile strength. The WTB is the area under the stress-strain curve. Toughness is the WTB normalized for the basis weight.

DuPont has relied solely upon high density polyethylene for all commercial operations in its Tyvek business and, indeed, the polyethylene used was specified from specific sources with very tight specifications. Recently, however, DuPont has begun to add post consumer recycled high density polyethylene to virgin polymer. The post consumer recycle is primarily from recycled milk jugs. Considerable engineering has gone into the system and process to accommodate the recycled materials, and the company is quite proud of this accomplishment.

With its new-found ability to accommodate what would have previously been considered very off-specification polyethylene, new types of polymer are being considered with the belief that new polymers may provide better economics of production or provide different product properties. It has now been found that polymer having a narrower range of molecular weight will actually provide considerably improved tensile strength, elongation and toughness. Until recently, high density

polyethylene was made by Ziegler-Natta heterogeneous solid catalyst systems. New polymer science and single-site catalyst systems bring opportunities and possibilities of polymers that have not been previously available. Such polymers made with single site catalyst systems, may have  
5 more consistent properties and perhaps specific molecular structures. DuPont has been experimenting with systems to fractionate conventional polymers into fractions having a very narrow molecular weight distribution and thereby provide polymer to its flash spinning systems which are relatively free of fractions which are less desirable in the final sheet  
10 products.

Although running new polymers such as those described above require considerable adjustment in the flash spinning process, it certainly appears that the polymer having a narrow molecular weight distribution may be flash spun into products that have considerably better properties in the  
15 very important areas of tensile strength, elongation and toughness.

The polymers that can be used for this invention include ethylene homo-polymers and copolymers, and blends of ethylene homo-polymers and copolymers. These polymers can be prepared by using either Ziegler-Natta type catalysts or single site catalysts. The polymers which are particularly  
20 useful for this invention are high density polyethylene (HDPE) made from ethylene homo-polymers or ethylene copolymers containing a relatively small amount of polymerized co-monomer units. Alpha olefins such as propylene, butene, hexene and octene are commonly used as a co-monomer for commercially available high density polyethylene copolymers. For  
25 purposes of clarity of meaning, in this application and especially in the claims, polyethylene shall mean a polymer comprised entirely or nearly entirely of ethylene monomer with no more than to a small portion of co-monomer units polymerized therein. High density polyethylene shall mean polyethylene having a density greater than about 0.935 g/cc.

30 One additional benefit of flash spinning narrow molecular weight distribution polymer is that much of the polymer that fouls the system is at the lower molecular weight range of the polymer that is provided into the system. Thus, it is anticipated that now that narrow molecular weight



distribution polyethylene can be flash spun that it may provide the benefit the system will suffer less fouling of the spin cell and possibly have longer, more stable runs of the system. Certainly, more production time would translate into better profit margins for the business.

5           Moreover, it has been found that tensile strength, elongation and toughness may be further improved by changing the shape of the spin orifice 14. The shape of the spin orifice 14 of particular interest is the length to diameter ratio. Referring to Figure 3, the spin orifice has a length identified by the letter  $l$  and a diameter identified by the letter  $d$ . The ratio of the  
10   length to diameter " $l/d$ " for the standard arrangement has historically been about one.

          With the standard arrangement, the polymer concentration has little effect on elongation and tensile strength. However, if the length to diameter ratio of the spin orifice 14 is sufficiently extended so that it is much  
15   longer than its diameter, the elongation of the flash-spun material can be substantially modified by adjustment of the ratio of polymer to spin agent in the homogeneous mixture being fed to the spin cell 10. Quite notably, the combination of spin orifice configuration, solution concentration and narrow molecular weight distribution polymer combine to provide considerably  
20   higher elongation and tensile properties.

          Example cases were prepared to illustrate the effects of changing the above described variables. However, it should be noted that other process conditions must be modified to be able to spin well fibrillated yarns which provide suitable sheets and sheet properties. In some situations, the  
25   amount of polymer available to test was not enough to make sheets. A small scale test device shown in Figure 4 is used to make flash-spun fiber which can be tested and compared to polymer samples made into both fiber and sheet.

          Turning now to Figure 4, there is illustrated a twin cell test device  
30   40 for mixing polymer and spin agent into a spin mixture. The device 40 comprises a block 41 which includes a primary cylinder chamber 44 and second cylinder chamber 45. Measured quantities of polymer and spin agent are provided into the primary cylinder chamber 44 through a suitable access

such as port 48. The polymer and spin agent are directed back and forth between the primary cylinder chamber 44 and the second cylinder chamber 45 through passage 50 which includes a static mixer element 51.

Pressurized fluid from a hydraulic pump 54 via hydraulic valve 55 and  
5 hydraulic lines 56 and 57 causes pistons 64 and 65 to move the polymer and spin agent between the two chambers 44 and 45. The mixture is heated to a predetermined temperature and the pressure is monitored at sensor 67 until the polymer and spin agent are adequately mixed. The hydraulic system is then operated to direct the solution into the primary cylinder chamber 44  
10 whereupon the valve 55 is closed to lock the secondary piston 65 closest to the passage 50. The hydraulic valve 55 is also closed to preclude hydraulic fluid from passing from line 56 back into the pump 54.

The spin solution now in the primary chamber 44 is spun through a valve 71 using an accumulator 74 to maintain relatively constant spin  
15 pressure. The accumulator 74 includes a relatively large cylinder 75 (compared to either of the primary and second cylinder chambers 44 and 45) with a piston 76. Hydraulic fluid (preferably water) fills a large portion of the accumulator cylinder 75, and pressurized gas fills the space inside cylinder 75 on the other side of the piston 76. The pressurized gas provided  
20 through a gas line 78 from a suitable source is controlled to create a nearly constant accumulator pressure during the spin which lasts a few seconds. The accumulator pressure is monitored at sensor 79. With the twin cell test device 40, there are several items to consider when comparing the operational parameters to the operation of the standard arrangement shown  
25 in Figure 1. The pressure letdown chamber disclosed by Anderson et al. (USP 3,227,794) was not used in the examples, and instead, the accumulator pressure is set at the end of the mixing cycle to the desired spin pressure to simulate the letdown chamber effect. Also, the valve 81 between the spin cell and the accumulator and the spinneret orifice 71 are opened in rapid  
30 succession. The resultant flash-spun product is collected in a stainless steel open mesh screen basket. Because of the relatively small amount of material and high pressure used, most of the spins in these Examples lasted for only about one second.

It usually takes about one to two seconds to open the spinneret orifice 71 after opening the valve 81 between the spin cell and the accumulator. When letdown chambers are used, the residence time in the chamber is usually 0.2 to 0.8 seconds. However, it has been determined that residence time does not have too much effect on fiber morphology and/or properties as long as it is greater than about 0.1 second but less than about 10 seconds. When the valve between the spin cell and the accumulator is opened, the pressure inside the spin cell drops immediately from the mixing pressure to the accumulator pressure. The spin cell pressure drops again when the spinneret orifice 71 is opened because of the pressure drop in the line 82. The pressure measured during spinning just before the spinneret with a pressure transducer using a computer is entered as the spin pressure in the examples. It is usually lower than the set accumulator pressure by about 100 to 200 psi. Therefore, the quality of the two phase dispersion in the spin cell depends on both the accumulator pressure and the actual spin pressure, and the time at those pressures. Sometimes the accumulator pressure is set at a pressure higher than the cloud point pressure. In this case, the quality of the two phase dispersion in the spin cell will be determined primarily by the spin pressure reached after the spinneret orifice is opened.

There are a number of tests and other measured parameters such as the tensile strength, break elongation, and toughness on yarn and sheets. Several measurements, tests and test methods are described hereafter to provide a brief description of a number of the tests and measured parameters.

#### Molecular Weight Distribution, Number Average Molecular Weight and Weight Average Molecular Weight

Weight average molecular weight and number average molecular weight were determined by gel permeation chromatography (GPC). The GPC analyses were performed on a Waters 150-C chromatograph equipped with three Polymer Labs Mixed B columns and a Viscotek viscosity detector. The solvent used to prepare the polymer solutions and also used as the mobile phase is 1,2,4-trichlorobenzene. Solution preparation and

analysis are done at 140 C. The system is calibrated against a series of narrow distribution polystyrenes.

Molecular weight distribution is the weight average molecular weight divided by the number average molecular weight.

5 Melt Index

Melt index is measured according to ASTM D1238-90A, which is hereby incorporated by reference, at a temperature of 190° C with a 2.16 kg weight and is expressed in units of g/10 minutes.

Concentration

10 Polymer/spin agent concentration is measured by weight percent.

Surface Area

Surface area for flash-spun polyethylene typically is in the range of 10 to 50 m<sup>2</sup>/gm. This is considerably higher than other fiber spinning technologies and provides the high opacity typically desired in nonwoven sheet products. The surface area of the plexifilamentary film-fibril strand is measured by the BET nitrogen absorption method of S. Brunauer, P. H. Emmett and E. Teller, J. Am. Chem. Soc., V. 60 p 309-319 (1938), which is hereby incorporated by reference, and is reported as m<sup>2</sup>/g. While surface area was not measured for the samples discussed below, based on visual observations by experienced personnel, it can be reported that all test below were within the typical surface area range for flash-spun polyethylene of 10 to 50 m<sup>2</sup>/gm.

Twin Cell Plexifilament Yarn Tensile Test Methods

Denier of the flash-spun strand is determined as follows: One 90 cm long strand of yarn is cut, and a weight of 100 grams is hung on one end of the yarn for 3 minutes to remove bends and waviness. From the long single yarn strand, five 18 cm individual pieces are cut, and denier is determined for each piece.

Tenacity, elongation and toughness of the strand are determined with an Instron tensile-testing machine. The strands are conditioned and tested at 70 F and 65 % relative humidity. The strands are then twisted to 10 turns per inch and mounted in the jaws of the Instron Tester. A two-inch

gauge length is used with an elongation rate of 2 inches per minute. The tenacity at break is recorded in grams per denier (gpd). The elongation at break is recorded as a percentage of the two-inch gauge length of the sample. Toughness is a measure of the work required to break the sample divided by the denier of the sample and is recorded in gpd. Modulus corresponds to the slope of the stress/strain curve and is expressed in units of gpd.

#### Basis Weight

Basis weight is determined by ASTM D3776, which is hereby incorporated by reference, and is reported in oz/yd<sup>2</sup> (g/m<sup>2</sup>). The basis weights reported for the examples below are each based on an average of at least six measurements made on the sheet.

#### Delamination Strength

Delamination strength of a sheet sample is measured using a constant rate of extension tensile testing machine such as an Instron table model tester. A 1.0 in. (2.54 cm) by 8.0 in. (20.32 cm) sample is delaminated approximately 1.25 in. (3.18 cm) by inserting a pick into the cross-section of the sample to initiate a separation and delamination by hand. The delaminated sample faces are mounted in the clamps of the tester which are set 1.0 in. (2.54 cm) apart. The tester is started and run at a cross-head speed of 5.0 in./min. (12.7 cm/min.). The computer starts picking up force readings after the slack is removed in about 0.5 in. of crosshead travel. The sample is delaminated for about 6 in. (15.24 cm) during which 3000 force readings are taken and averaged. The average delamination strength is the average force divided by the sample width and is expressed in units of lbs/in (N/cm). The test generally follows the method of ASTM D2724-87, which is hereby incorporated by reference. The delamination strength values reported for the examples below are each based on an average of at least six measurements made on the sheet.

#### Opacity

Opacity is measured according to TAPPI T-519 om-86, which is hereby incorporated by reference. The opacity is the reflectance from a

single sheet against a black background compared to the reflectance from a white background standard and is expressed as a percent. The opacity values reported for the examples below are each based on an average of at least six measurements made on the sheet.

5 Grab Tensile

Tensile properties are determined by ASTM D1682, Section 19, which is hereby incorporated by reference, with the following modifications. In the test a 2.54 cm by 20.32 cm (1 inch by 8 inch) sample was clamped at opposite ends of the sample. The sample was pulled steadily at a speed of  
10 5.08 cm/min (2 in/min) until the sample broke. The tensile property values reported for the examples below were each an average of six measurements on specimens cut in the machine direction and six measurements on specimens cut in the cross direction. The force at break was normalized by dividing by the samples basis weight and was recorded in lb-yd<sup>2</sup>/(oz-in)  
15 (N-m<sup>2</sup>/(g-cm)) as the breaking strength. The elongation at 13.34 Newtons (3 lb) load and the elongation at break were recorded as a percent of the original sample length. The Work-to-Break (WTB), which is the area under the stress-strain curve, was normalized by dividing by the sample basis weight and the sample width and is reported as toughness in lb-yd<sup>2</sup>/oz  
20 (N-m<sup>2</sup>/g).

Spencer Puncture

Spencer puncture is measured according to ASTM D3420-91 Procedure B, which is hereby incorporated by reference, with the exception that an impact head with contact area of 0.35 square inches was used on a  
25 modified Elmendorf tester having a capacity of 6400 gram-force. Results are normalized by dividing the measured energy to rupture by the area of the impact head and are reported in in-lbs/in<sup>2</sup> (J/cm<sup>2</sup>). The results below are each based on an average of at least six measurements on the sheet.

Elmendorf Tear

30 Elmendorf tear strength is measured according to ASTM D1424, which is hereby incorporated by reference. The Elmendorf tear values are reported for the examples below.

With the twin cell system 40 of Figure 4, a large number of polymer tests have been run providing data that can be used to predict properties in the sheet products. In Examples Y-1a through Y-D3, the spin agent comprises 68% normal pentane and 32% cyclopentane. Focusing on flash-spun yarn properties the following examples were run in the twin cell system 40 with the following properties:

	<u>Con. Y-1a</u>	<u>Con. Y-1b</u>	<u>Con. Y-1c</u>	<u>Con. Y-1d</u>
<u>Polymer</u>				
Number Average Molecular Weight	22,000	22,000	22,000	22,000
Weight Average Molecular Weight	124,000	124,000	124,000	124,000
Molecular Weight Distribution	5.5	5.5	5.5	5.5
Melt Index (g/10 min)	0.67	0.67	0.67	0.67
Density (g/cc)	0.96	0.96	0.96	0.96
<u>Spin Conditions</u>				
Concentration (%)	18	18	18	18
Temperature (°C)	186	185	185	185
Spin pressure (psig)	875	800	800	750
Accum. Pressure (psig)	1100	1000	950	900
<u>Properties</u>				
Denier	180	183	218	214
Modulus (gpd)	17.7	18.6	15.2	16.2
Tenacity (gpd)	4.82	5.75	5.08	5.27
Toughness (gpd)	1.62	2.91	2.82	2.58
Elongation (%)	53.9	74.5	87.4	77.4



	<u>Con. Y-1e</u>	<u>Ex. Y-A1</u>	<u>Ex. Y-A2a</u>	<u>Ex. Y-A2b</u>
<u>Polymer</u>				
Number Average Molecular Weight	22,000	47,000	27,800	27,800
Weight Average Molecular Weight	124,000	97,800	106,800	106,800
Molecular Weight Distribution	5.5	2.08	3.84	3.84
Melt Index (g/10 min)	0.67	0.77	1.56	1.56
Density (g/cc)	0.96	0.953	0.959	0.959
<u>Spin Conditions</u>				
Concentration (%)	18	18	18	18
Temperature (°C)	185	185	186	185
Spin pressure (psig)	650	1025	1000	950
Accum. Pressure (psig)	800	1100	1100	1000
<u>Properties</u>				
Denier	185	152	164	185
Modulus (gpd)	14	12	12.3	10.9
Tenacity (gpd)	4.43	3.71	4.33	3.88
Toughness (gpd)	2.37	3.88	3.43	3.17
Elongation (%)	82.8	152	117	122

	<u>Ex. Y-A3</u>	<u>Ex. Y-A4</u>	<u>Ex. Y-A5a</u>	<u>Ex. Y-A5b</u>
<u>Polymer</u>				
Number Average Molecular Weight	40,200	35,600	46,500	46,500
Weight Average Molecular Weight	127,800	121,800	120,200	120,200
Molecular Weight Distribution	3.18	3.42	2.58	2.58
Melt Index (g/10 min)	0.8	0.7	0.75	0.75
Density (g/cc)	0.955	0.954	0.955	0.955
<u>Spin Conditions</u>				
Concentration (%)	18	18	18	18
Temperature (°C)	185	185	185	185
Spin pressure (psig)	1100	1000	875	750
Accum. Pressure (psig)	1200	1100	1000	900
<u>Properties</u>				
Denier	155	155	201	203
Modulus (gpd)	12.1	16.1	11.9	9.85
Tenacity (gpd)	5.36	5.39	4.5	4.01
Toughness (gpd)	3.29	3.37	3.65	3.51
Elongation (%)	96	94	118	129

	<u>Ex. Y-A5c</u>	<u>Ex. Y-B1a</u>	<u>Ex. Y-B1b</u>	<u>Ex. Y-B1c</u>
<u>Polymer</u>				
Number Average Molecular Weight	46,500	49,500	49,500	49,500
Weight Average Molecular Weight	120,200	130,900	130,900	130,900
Molecular Weight Distribution	2.58	2.65	2.65	2.65
Melt Index (g/10 min)	0.75	0.75	0.75	0.75
Density (g/cc)	0.955	0.949	0.949	0.949
<u>Spin Conditions</u>				
Concentration (%)	20	18	18	18
Temperature (°C)	184	185	186	185
Spin Pressure (psig)	600	1100	1050	950
Accum. Pressure (psig)	750	1250	1200	1050
<u>Properties</u>				
Denier	194	162	195	174
Modulus (gpd)	10.8	8.79	9.09	8.88
Tenacity (gpd)	4.05	5.32	3.3	92.1
Toughness (gpd)	3.34	3.3	3.85	3.6
Elongation (%)	122	92.1	121	122

	<u>Ex. Y-C1</u>	<u>Ex. Y-C2</u>	<u>Ex. Y-C3</u>	<u>Ex. Y-C4</u>
<u>Polymer</u>				
Number Average Molecular Weight	45,000	29,900	51,700	81,700
Weight Average Molecular Weight	172,000	122,000	166,000	204,000
Molecular Weight Distribution	3.83	4.09	3.21	2.5
Melt Index (g/10 min)	0.14	0.66	0.24	0.12
Density (g/cc)	0.9544	0.9582	0.9531	0.9477
<u>Spin Conditions</u>				
Concentration (%)	18	18	18	18
Temperature (°C)	186	185	185	185
Spin Pressure (psig)	950	950	1125	1100
Accum. Pressure (psig)	1050	1050	1250	1225
<u>Properties</u>				
Denier	157	154	190	172
Modulus (gpd)	14.1	11.3	9.29	12.1
Tenacity (gpd)	5.4	3.9	5.5	5.66
Toughness (gpd)	3.11	3.3	5.03	3.14
Elongation (%)	87	132	128	96

	<u>Ex. Y-C5</u>	<u>Ex. Y-C6</u>	<u>Ex. Y-D1</u>
<u>Polymer</u>			
Number Average Molecular Weight	36,300	37,600	45,000
Weight Average Molecular Weight	104,200	105,200	80,800
Molecular Weight Distribution	2.87	2.8	1.79
Melt Index (g/10 min)	0.778	0.778	nm
Density (g/cc)	0.95	0.95	nm
<u>Spin Conditions</u>			
Concentration (%)	18	18	18
Temperature (°C)	185	185	185
Spin Pressure (psig)	1050	975	950
Accum. Pressure (psig)	1175	1050	1050
<u>Properties</u>			
Denier	175	152	138
Modulus (gpd)	14.2	11.3	6.42
Tenacity (gpd)	5.39	4.81	1.68
Toughness (gpd)	3.31	3.46	3.4
Elongation (%)	98	107	303

nm - not measured

	<u>Ex. Y-D2</u>	<u>Ex. Y-D3</u>
<u>Polymer</u>		
Number Average Molecular Weight	69,033	128,900
Weight Average Molecular Weight	114,200	242,800
Molecular Weight Distribution	1.65	1.88
Melt Index (g/10 min)	nm	nm
Density (g/cc)	nm	nm
<u>Spin Conditions</u>		
Concentration (%)	18	15
Temperature (°C)	185	185
Spin Pressure (psig)	975	1200
Accum. Pressure (psig)	1050	1350
<u>Properties</u>		
Denier	124	150
Modulus (gpd)	1.5	10.6
Tenacity (gpd)	3.52	4.29
Toughness (gpd)	3.25	4.22
Elongation (%)	134	144

nm - not measured

Tests have also been run on pilot line equipment to make sheet products. On the pilot line for Example S-B1a, plexifilamentary polyethylene was flash spun from a solution consisting of 18.1% of linear high density polyethylene and 81.9% of a spin agent consisting of 32% cyclopentane and 68% normal pentane. The polyethylene had a melt index of 0.73 g/10 minutes (@ 190°C with a 2.16 kg weight), a melt flow ratio {MI(@ 190°C with a 2.16 kg weight)/MI (@190°C with a 21.6 kg weight)} of 34, and a density of 0.96 g/cc. The polyethylene was obtained from Lyondell Petrochemical Company of Houston, Texas under the tradename ALATHON®. ALATHON® is currently a registered trademark of Lyondell Petrochemical Company. The solution was prepared in a continuous mixing unit and delivered at a temperature of 185°C, and a pressure of about 13.8 MPa (2000 psi) through a heated transfer line to an array of six spinning positions. Each spinning position has a pressure letdown chamber where the solution pressure was dropped to about 7.0 MPa (1010 psi). The solution was discharged from each letdown chamber to a region maintained near atmospheric pressure and at a temperature of about 50°C through a 0.871 mm(0.0343 in) spin orifice having a length to diameter of about 0.9. The flow rate of solution through each orifice was about 136 kg/hr (299 lbs/hr). The solution was flash spun into plexifilamentary film-fibrils that were laid down onto a moving belt, consolidated, collected as a loosely consolidated sheet on a take-up roll as described above.

The sheet was bonded on a Palmer bonder by passing the sheet between a moving belt and a rotating heated smooth metal drum with a diameter of about five feet. The drum is heated with pressurized steam and the bonding temperature is controlled by adjusting the pressure of the steam inside the drum. The pressurized steam heats the bonding surface of the drum to approximately 133 to 141°C. The pressure of the steam is used to adjust the temperature of the drum according to the degree of bonding desired. The bonded sheet has the opacity, delamination and other properties as set forth in the following Table as Example S-B1a. Examples S-B1b through C-Sheet were created manner similar to S-B1a with differences as noted.

It should be noted that properties of the sheet vary as the bonding temperature is changed by adjusting the bonder steam pressure. Normally, delamination strength increases and opacity decreases as bonding temperature is increased. The bonding temperature required to attain a specified level of delamination strength or opacity depends on the polymer and spinning conditions used to make the unbonded precursor sheet. In order to make meaningful comparisons among samples, each of the sheet samples below were bonded over a range of temperatures yielding delamination strength values both less than and greater than 0.35 lb/in, and the properties at 0.35 lb/in delamination strength were then estimated using linear regression.



	<u>Ex. S-B1a</u>	<u>Ex. S-B1b</u>	<u>Ex. S-B2</u>
<u>Polymer</u>			
Number Average Molecular Weight	25,033	25,033	49,500
Weight Average Molecular Weight	143,467	143,467	130,900
Molecular Weight Distribution	5.73	5.73	2.65
Melt Index (g/10 min)	0.73	0.73	0.75
Density (g/cc)	0.960	0.960	0.949
<u>Spin Conditions</u>			
Concentration (%)	18.1	17.7	17.2
Temperature (°C)	185	185	185
Letdown pressure (psig)	1010	960	1100
Spin Orifice L/D Ratio	0.9	0.9	0.9
Bonding Pressure (psia)	49.8	49.4	48.4
<u>Properties</u>			
Opacity (%)	96.9	97.5	97.5
Basis Weight (oz/yd <sup>2</sup> )	1.7	1.7	1.7
Break Strength (lb yd <sup>2</sup> /oz·in)	18.1	17.4	17.0
Break Elongation (%)	16.3	14.5	36.2
Toughness (lbs·yd <sup>2</sup> /oz)	9.5	8.1	19.8
Elmendorf Tear (lbs)	1.6	1.9	1.4
Spencer Puncture (in-lbs/in <sup>2</sup> )	22.0	27.1	51.3

	<u>Ex. S-B3a</u>	<u>Ex. S-B3b</u>	<u>Ex. S-B4</u>	<u>Ex. S-B5</u>
<u>Polymer</u>				
Number Average Molecular Weight	25,200	25,200	35,600	40,200
Weight Average Molecular Weight	155,200	155,200	121,800	127,800
Molecular Weight Distribution	6.15	6.15	3.42	3.18
Melt Index (g/10min)	0.67	0.67	0.70	0.80
Density (g/cc)	0.961	0.961	0.954	0.955
<u>Spin Conditions</u>				
Concentration (%)	17.8	18.2	17.8	17.5
Temperature (°C)	180	180	180	180
Letdown pressure (psig)	910	900	910	920
Spin Orifice L/D Ratio	0.9	0.9	0.9	0.9
Bonding Pressure (psia)	46.2	47.0	50.8	49.0
<u>Properties</u>				
Opacity (%)	97.6	97.2	96.7	97.0
Basis Weight (oz/yd <sup>2</sup> )	1.7	1.7	1.7	1.8
Break Strength (lbs-yd <sup>2</sup> /oz)	17.3	18.9	19.8	16.7
Break Elongation (%)	17.4	15.7	27.3	22.7
Toughness (lbs-yd <sup>2</sup> /oz)	9.8	9.7	16.7	12.2
Elmendorf Tear (lbs)	1.6	1.5	1.7	1.9
Spencer Puncture (in-lbs/in <sup>2</sup> )	27.6	25.1	33.2	27.9

	<u>Ex. S-B6</u>	<u>Ex. S-B7a</u>	<u>Ex. S-B7b</u>	<u>Ex. S-B8</u>
<u>Polymer</u>				
Number Average Molecular Weight	47,000	24,700	25,400	41,400
Weight Average Molecular Weight	97,760	156,400	153,000	94,400
Molecular Weight Distribution	2.08	6.34	6.03	2.28
Melt Index (g/10 min)	0.77	.754	0.73	0.840
Density (g/cc)	0.953	0.9617	0.9615	0.9530
<u>Spin Conditions</u>				
Concentration (%)	18.7	17.9	17.8	16.9
Temperature (°C)	180	185	185	185
Letdown pressure (psig)	900	980	1020	980
Spin Orifice L/D Ratio	0.9	0.9	0.9	0.9
Bonding Pressure (psia)	44.9	47.9	48.4	47.5
<u>Properties</u>				
Opacity (%)	97.3	97.6	97.9	96.7
Basis Weight (oz/yd <sup>2</sup> )	1.6	1.7	1.7	1.7
Break Strength (lbs·yd <sup>2</sup> /oz)	12.2	16.9	16.2	10.2
Break Elongation (%)	31.0	15.0	14.5	40.0
Toughness (lbs·yd <sup>2</sup> /oz)	13.5	8.4	7.8	14.2
Elmendorf Tear (lbs)	1.7	1.5	1.7	1.3
Spencer Puncture (in-lbs/in <sup>2</sup> )	21.0	21.8	25.8	23.9

	Ex. B9a	Ex. B9b
<b><u>Polymer</u></b>		
Number Average Molecular Weight	46,500	46,500
Weight Average Molecular Weight	120,200	120,200
Molecular Weight Distribution	2.58	2.58
Melt Index (g/10 min)	0.75	0.75
Density (g/cc)	0.955	0.955
<b><u>Spin Conditions</u></b>		
Concentration (%)	18.2	18.4
Temperature (°C)	185	185
Letdown pressure (psig)	1100	1030
Spin Orifice L/D Ratio	0.9	0.9
Bonding Pressure (psia)	47.5	48.5
<b><u>Properties</u></b>		
Opacity (%)	97.2	97.9
Basis Weight (oz/yd <sup>2</sup> )	1.8	1.8
Break Strength (lbs·yd <sup>2</sup> /oz)	13.4	14.2
Break Elongation (%)	21.1	20.8
Toughness (lbs·yd <sup>2</sup> /oz)	9.3	9.9
Elmendorf Tear (lbs)	1.8	2.5
Spencer Puncture (in-lbs/in <sup>2</sup> )	23.8	32.8

In the following example, the yarn was collected from the unconsolidated sheet from the system described for making Example S-B1a.

<u>Ex. C Yarn</u>	
<u>Polymer</u>	
Number Average Molecular Weight	49,500
Weight Average Molecular Weight	130,900
Molecular Weight Distribution	2.65
Melt Index (g/10 min)	0.75
Density (g/cc)	0.949
<u>Spin Conditions</u>	
Concentration (%)	17.9
Temperature (°C)	185
Letdown pressure (psig)	1020
Spin Orifice L/D Ratio	4.1
Denier	279
<u>Twisted Web</u>	
Modulus (gpd)	4.3
Tensile Strength (gpd)	2.6
Elongation (%)	205
<u>Untwisted Web</u>	
Modulus (%)	3.8
Tensile Strength (gpd)	1.4
Break Elongation (%)	74

Ex. C SheetPolymer

Number Average Molecular Weight	49,500
Weight Average Molecular Weight	130,900
Molecular Weight Distribution	2.65
Melt Index (g/10 min)	0.75
Density (g/cc)	0.949

Spin Conditions

Concentration (%)	17.9
Temperature (°C)	185
Letdown pressure (psig)	1020
Spin Orifice L/D Ratio	4.1

Properties

Delamination	0.35
Opacity (%)	95
Break Strength (lbs·yd <sup>2</sup> /oz)	15
Break Elongation (%)	47
Toughness (lbs·yd <sup>2</sup> /oz)	38
Elmendorf Tear (lbs)	1.1
Spencer Puncture (in-lbs/in <sup>2</sup> )	25

- 5 In summary, flash spinning narrow molecular weight distribution polyethylene yields improved qualities, especially in tensile strength, elongation and toughness. Additional improvements in elongation may also be attained by changes in the spin orifice geometry and in the spin

concentration. Notably, each of these changes, polymer and spin conditions, improve the properties of the product independently of the other. In other words, each can be adjusted individually to improve the properties and both can be adjusted together to improve them the most.

- 5           The foregoing description and drawings were intended to explain and describe the invention so as to contribute to the public base of knowledge. In exchange for this contribution of knowledge and understanding, exclusive rights are sought and should be respected. The scope of such exclusive rights should not be limited or narrowed in any way
- 10 by the particular details and preferred arrangements that may have been shown. Clearly, the scope of any patent rights granted on this application should be measured and determined by the claims that follow.

## WE CLAIM:

1. A polyethylene flash-spun plexifilamentary yarn having a BET surface area of greater than  $2 \text{ m}^2/\text{gm}$  wherein the polymer has a number average molecular weight of at least about 20,000 and a molecular weight distribution of less than about 4.0.
2. The polyethylene plexifilamentary yarn according to Claim 1 wherein the molecular weight distribution of the polymer is less than about 3.0.
3. The polyethylene plexifilamentary yarn according to Claim 1 wherein the break elongation of the yarn is greater than about 100 percent.
4. The polyethylene plexifilamentary yarn according to Claim 1 wherein the toughness of the yarn is greater than about 3 grams per denier.
5. The polyethylene plexifilamentary yarn according to Claim 1 wherein the polyethylene is high density polyethylene.
6. A nonwoven sheet comprising flash-spun polyethylene plexifilamentary yarn having a BET surface area of greater than  $2 \text{ m}^2/\text{gm}$  wherein the polyethylene has a number average molecular weight of at least about 20,000 and a molecular weight distribution of less than about 4.0.
7. The nonwoven sheet according to Claim 6 wherein the molecular weight distribution of the polyethylene polymer is less than about 3.0.
8. A nonwoven sheet comprising polyethylene flash-spun plexifilamentary film-fibrils wherein the plexifilaments are bonded together across the area of the sheet and wherein the polyethylene has a number average molecular weight greater than about 20,000 and a molecular weight distribution of less than about 4.0.



9. The nonwoven sheet according to Claim 8 wherein the basis weight is less than about 3.0 ounces per square yard and the delamination strength is between about 0.20 and about 0.75 pounds per inch and the opacity is greater than about 85%.

5 10. The nonwoven sheet according to Claim 8 wherein the break elongation is at least 20 percent.

11. The nonwoven sheet according to Claim 8 wherein the sheet is area bonded and has a measurable delamination strength and further wherein the toughness is greater than about seven lbs-yd<sup>2</sup>/oz plus 13.5 times  
10 the delamination strength measured as lb/in.

12. The nonwoven sheet according to Claim 11 wherein the toughness is greater than about 10 lbs-yd<sup>2</sup>/oz plus 13.5 times the delamination strength measured as lb/in.

13. A polymeric nonwoven sheet comprising flash-spun  
15 plexifilaments wherein the break elongation is greater than 25%.

14. The polymeric nonwoven sheet according to Claim 13 wherein the break elongation is greater than 35%.

15. The polymeric nonwoven sheet according to Claim 13 wherein the break elongation is greater 45%.

20 16. The polymeric nonwoven sheet according to Claim 13 wherein the sheet is area bonded.

17. The polymeric nonwoven sheet according to Claim 13 wherein the sheet is point bonded across the area of the sheet.

25 18. The nonwoven sheet according to Claim 13 having an opacity of at least 90% and a delamination strength of at least about 0.20 pounds per inch.

19. A polyethylene flash-spun plexifilamentary film-fibril material wherein the polyethylene has a number average molecular weight of at least 20,000 and a molecular weight distribution of less than about 4.0, and wherein the film-fibril material has a BET surface area greater than 2 m<sup>2</sup>/gm.

20. The film-fibril material according to Claim 19 wherein the molecular weight distribution of the polyethylene is less than about 3.5.

21. The film-fibril material according to Claim 19 wherein the molecular weight distribution of the polyethylene is less than about 3.0.

22. The film-fibril material according to Claim 19 wherein the molecular weight distribution of the polyethylene is less than about 2.5.

23. The nonwoven sheet according to Claim 19 wherein the sheet is area bonded and has a measurable delamination strength and further wherein the toughness is greater than about seven lbs-yd<sup>2</sup>/oz plus 13.5 times the delamination strength measured as lb/in.

24. The nonwoven sheet according to Claim 23 wherein the toughness is greater than about 10 lbs-yd<sup>2</sup>/oz plus 13.5 times the delamination strength measured as lb/in.

25. A process for flash spinning high elongation flash-spun products wherein the process comprises the steps of forming a solution of polymer and spin liquid at elevated pressure and temperature, wherein the polymer is selected to have a molecular weight distribution of less than about 4.0, and flash spinning the solution through an orifice having a length to diameter of greater than about 2.0 to form plexifilamentary film-fibril material having a yarn break elongation of greater than 100%.

26. The process according to Claim 25 wherein the process further comprises spinning the solution through a spin orifice with an length to diameter ratio of at least about 3.0.

27. The process according to Claim 25 wherein the process further comprises forming a solution of polymer and spin liquid wherein the polymer has a molecular weight distribution of less than about 3.5.

5 28. The process according to Claim 27 wherein the polyethylene is fractionated prior to the solutioning step wherein portions of the polyethylene are separated to reduce the molecular weight distribution of the polyethylene that is flash-spun into plexifilamentary film-fibril material.

10 29. A nonwoven sheet comprising polyethylene flash-spun plexifilamentary film-fibrils wherein the plexifilaments are bonded together across the area of the sheet and wherein the polyethylene has a number average molecular weight greater than about 20,000 and a molecular weight distribution of less than about 4.0.

15 30. The nonwoven sheet according to Claim 29 wherein the basis weight is less than about 3.0 ounces per square yard and the delamination strength is between about 0.20 and about 0.75 pounds per inch and the opacity is greater than about 85%.

31. The nonwoven sheet according to Claim 29 wherein the break elongation is at least 20 percent.

20 32. The nonwoven sheet according to Claim 29 wherein the toughness is at least about 8.

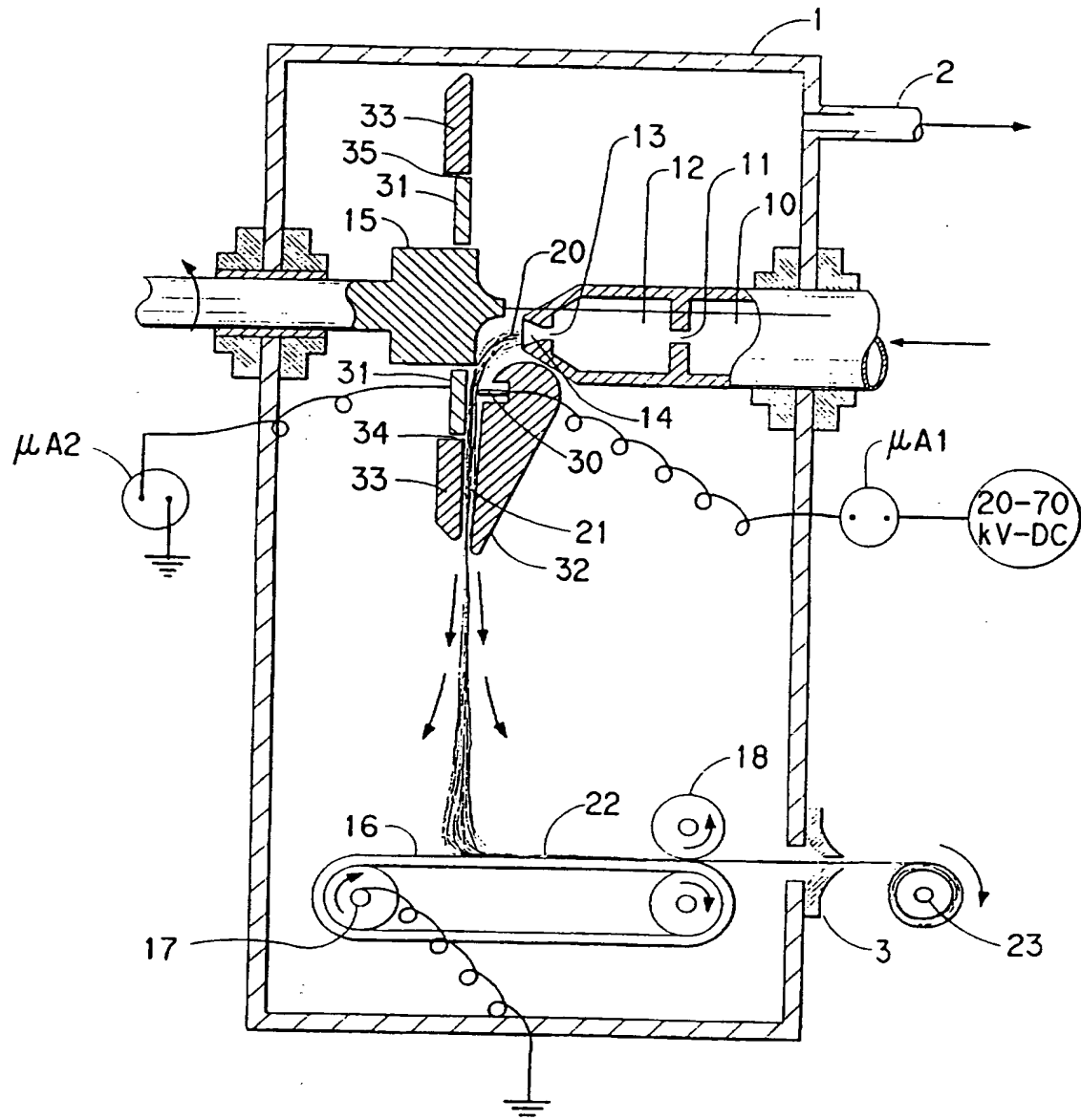


FIG. 1

**SUBSTITUTE SHEET (RULE 26)**

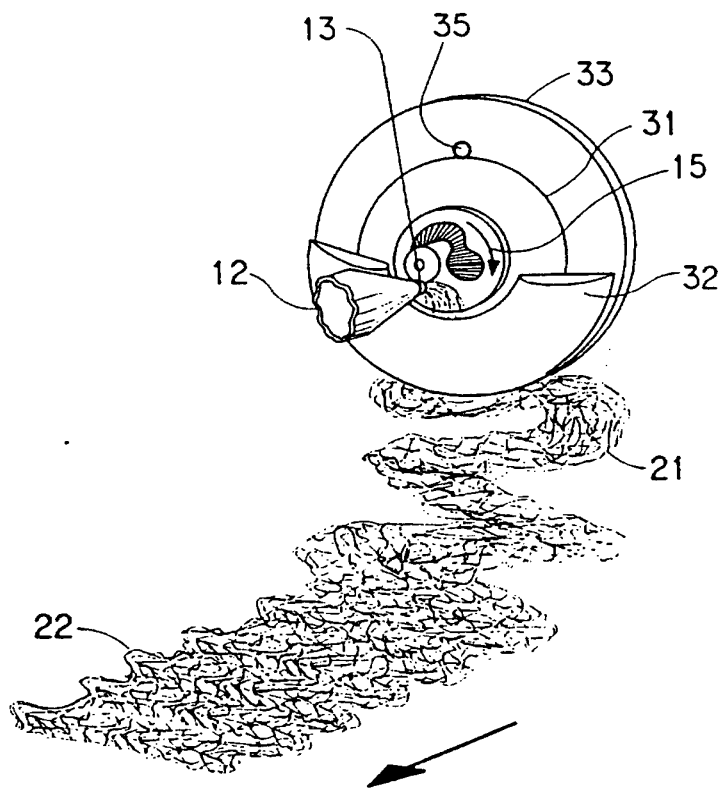


FIG. 2

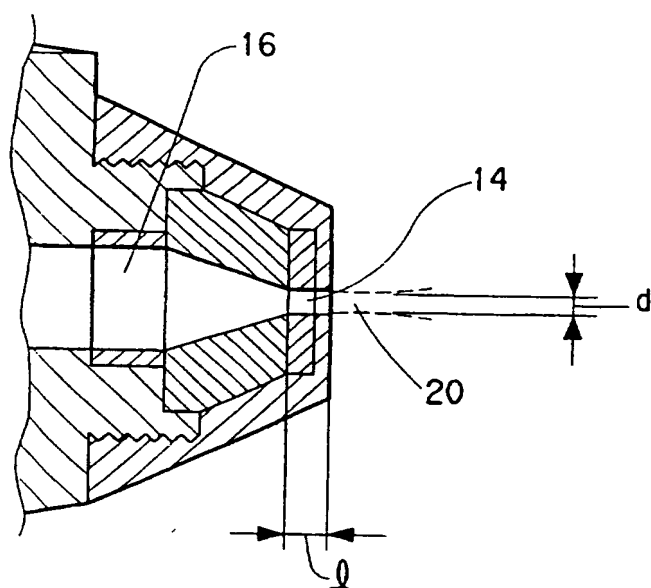


FIG. 3

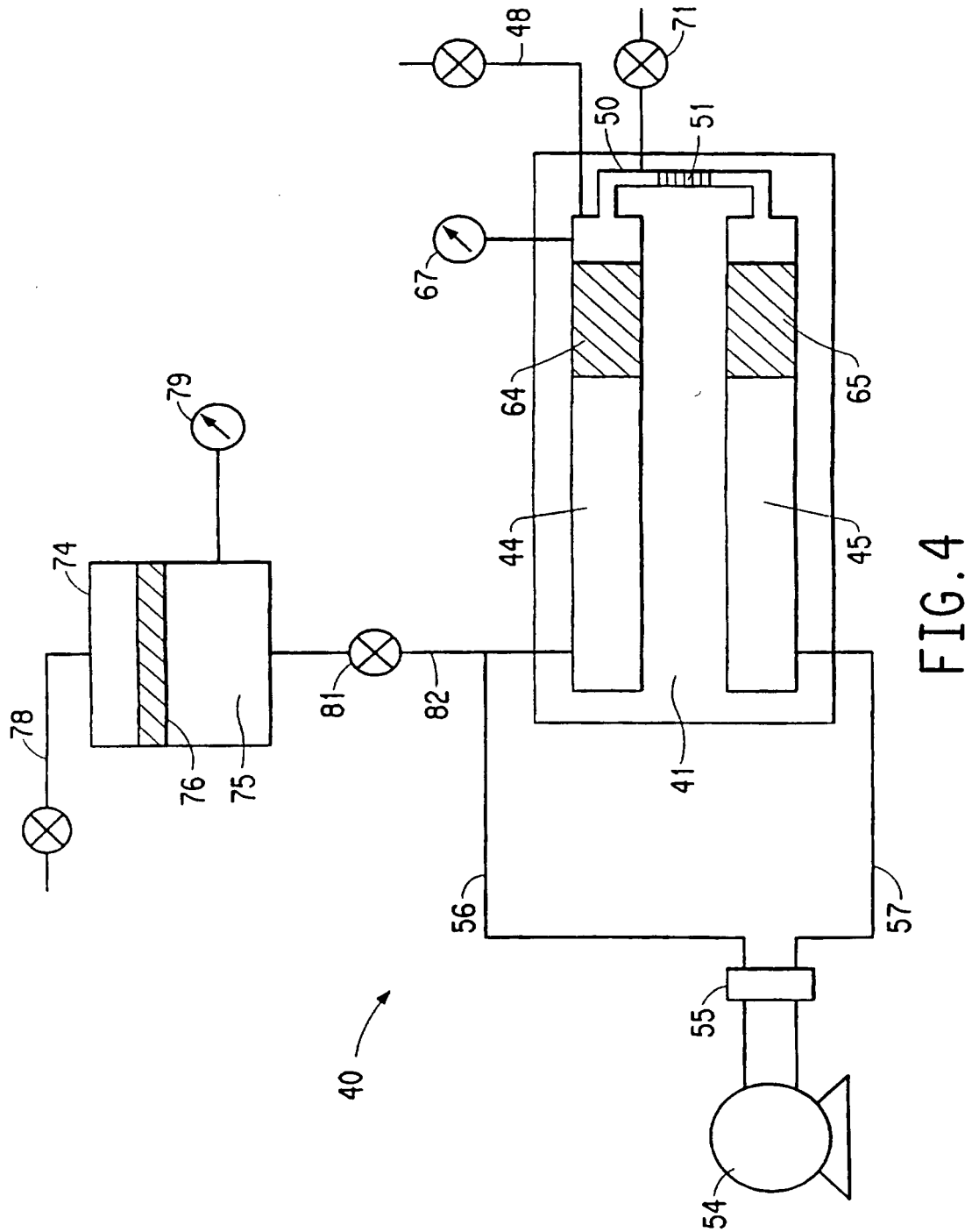


FIG. 4

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 97/14513

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 D01D5/11 D04H3/16 D01F6/04

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 D01D D04H D01F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 250 237 A (SHIN HYUNKOOK) 5 October 1993  see column 2, line 44 - line 47 see column 5, line 28 - line 33 see column 9, line 21 - line 27 see column 9, line 42 - line 47 see column 9, line 59 - line 60; tables 1,3  ---	1,5,6,8, 13,19, 25,29
A	US 4 554 207 A (LEE CHI C) 19 November 1985 see column 3, line 46 - line 47; claim 1  ---	1,6,8,9, 18
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-/--		

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents :

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- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*&\* document member of the same patent family

Date of the actual completion of the international search

20 November 1997

Date of mailing of the international search report

10. 12. 97

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# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 97/14513

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Information on patent family members

International Application No

PCT/US 97/14513

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